"EFFECT OF SURFACTANT ON EVAPORATION OF WATER"

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In partial fulfillments of the requirements of

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By

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2012

National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"EFFECT OF SURFACTANT ON EVAPORATION OF WATER"** submitted by **Shri Rupam Ranjan Biswal** in partial fulfillments for the requirement for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology Rourkela (Deemed University) is an authentic work carried out by him under supervision and guidance.

To best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institution for the award of any Degree or Diploma.

Date:07/05/2012

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Date: RUPAM RANJAN BISWAL

CONTENTS

ABSTRACT

The effect of surfactants on the evaporation of water was studied. Two different surfactants, cationic cetyltrimethylammonium Bromide (CTAB) and anionic Sodium Lauryl Sulphate (SLS) were used for this study. Experiments were carried out for different concentrations of CTAB and SLS. Water loss was found to decrease in presence of surfactants and with increasing the concentration of surfactant. Water loss was comparatively less in the presence of the cationic surfactant CTAB than in case of the anionic surfactant SLS. The effect of electrolyte (NaCl) on evaporation in the presence of both surfactants was also studied and the results show in the presence of electrolytes the evaporation increases compare to the pure surfactant solution. The evaporation of the water is totally depends on the packing of the monomer surfactant molecules at the air-water interface, so the evaporation is decreases in the surfactant solution as monomer surfactant molecules adsorbed in the air-water interface which creates an extra resistance to evaporation.

Key words: Evaporation, surfactant, electrolyte, critical micellar concentration (CMC)

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Chapter 1

Introduction

1. Introduction

1.1.1 Evaporation of water

Evaporation is a type of vaporization of liquid that occurs only on the surface of a liquid. The molecule in a glass of water does not have enough heat energy to escape from the liquid. When molecules collide with each other they transfer energy to each other. Sometimes this transfer provides enough energy to escape from surface. For the evaporation of water one of the major factors is humidity. Humidity refers to the amount of water vapor in the air. It is affected by temperature, wind and rainfall. Relative humidity depends on water vaporization and condensation which is mainly depends on temperature. When applying more pressure to a gas saturated with water, all components will initially decrease in volume according to ideal gas [1].

If in a closed vessel the evaporation occurs then the vapor molecules converted to the liquid, because of the increase in the density and pressure of the vapor. The rate of evaporation depends on the following factors.

Concentration: Evaporation is mostly dependent upon the concentration gradient between the evaporating liquid and its concentration in the surrounding environment. Higher the concentration gradient higher the evaporation and vice versa

Inter molecular force: Higher the intermolecular forces of attraction between the liquid molecules, higher energy is required to escape from surface.

Pressure: Rate of molecule getting evaporated is also dependent upon the Force acting on it. If the pressure on the surface is more, then the molecules have to overcome this extra force to come out of the surface

Surface Area: Evaporation directly depends on the exposed surface area as there are more surface molecules that are able to escape.

1.1.2 **Brief introduction to Surfactants**

The surfactant or "surface-active-agent" represents a heterogeneous and a long chain molecule containing both hydrophilic and hydrophobic moieties [2].

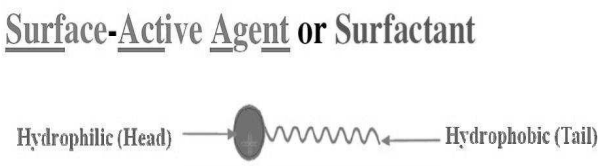

Figure 1.2. Schematic diagram of surfactant molecules

1.3 Types of surfactants

There are different types of surfactants which have very unique properties and characteristic. Depending on each type of charge of the head, a surfactant belongs to the anionic, cationic, non-ionic or amphoteric/zwitterion family [2].

1.3.1 Anionic Surfactant

In the solution, the head is negatively charged. This surfactant is most widely used in laundering, dishwashing liquids and shampoos because of its excellent cleaning properties. The most commonly used anionic surfactant is alkyl sulphates, alkyl ethoxylatesulphates and soap.

1.3.2 Cationic Surfactant

In solution, the head is positively charged. In fabric softener and in detergents with build-in fabric softener, cationic surfactant provides softness. The main use in laundry products is in rinse added fabric softener, such as esterquets. Most commonly cationic surfactant are esterquets. In laundry detergent cationic surfactants improves the packing of anionic surfactant molecules at the stain/water interface.

1.3.3 Non-ionic Surfactant

These surfactants do not have any electrical charges, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dishwashing liquids. Most laundry detergents contain both non-ionic and anionic surfactant as they complement each other's cleaning action [2].

1.4 Electrolytes

Electrolytes are ionic compounds that easily dissociates in aqueous solution. The presence of electrolytes in the surfactant aqueous solution decreases the CMC and increases the aggregation number. The lower of the CMC is due to the reduction in the electrostatic repulsion between the head group. Near the CMC the surfactant concentration usually found the solubilizing power of a system increasing the addition of electrolyte, so that greater number micelle will form. [3]

1.5 Applications

- A detergent is a surfactant or a mixture of surfactants with cleaning properties in dilute solutions
- Cosmetics are substances used to enhance the appearance or odor of the human body.

Chapter 2

Literature Review

2.1 Introduction

The evaporation of a water droplet is not only important for the different heat transfer applications but it is also associated with common everyday phenomena, such as for printing, washing, coating, and foliar fertilizer delivery. Transport properties such as evaporation rates are of interest in the assessment of hazards arising from volatile chemicals in drying processes (e.g., during preparation of powders), and in the release of volatile active species such as perfumes and flavors from commercial products. Very few reports exist in the literature on the evaporation rate of water. Rate of evaporation of water droplet depends on various factors like relative humidity, temperature, additives such as surfactant, electrolytes, alcohols etc. [4].

2.2. Effect of surfactant on evaporation of water

There are some studies documented on the drying mechanism of surfactant solutions by gravimetrically monitoring the water loss in air and controlled relative humidity.

The evaporation rates of PTFE marbles formed by encapsulating PTFE micropowder on a water droplet in a closed chamber where relative humidity and temperature was kept constant was investigated by Tosun et al. [5] Evaporation rates of PTFE marbles were compared with the rates of pure water droplets in terms of evaporation resistance, Φ and it was found that PTFE marbles have longer life-time than water droplets so that Φ values were found to increase regularly from 0.365 to 0.627 with the increase of RH of the evaporating medium. They also shown the water loss at different constant relative humidity (RH) and results shows that with increase in RH water loss decreases as shown in Figure 2.1 and the rate of water loss is maximum in the 5% RH environment.

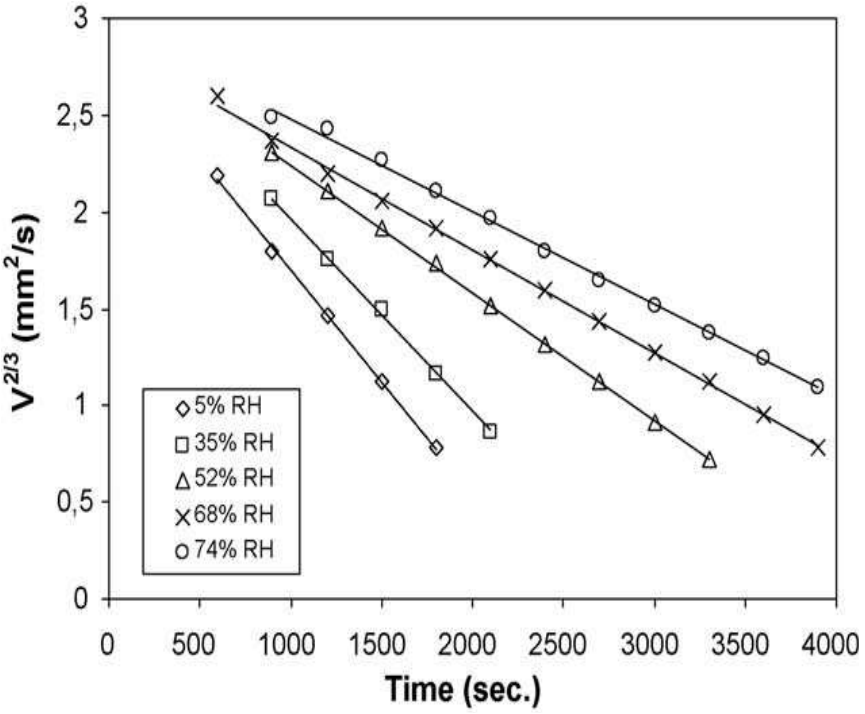

Fig. 2.1.$V^{2/3}$ v/s .time plot of 5 ml pure water droplets during evaporation in the closed chamber at constant relative humidity (RH = 5, 35, 52, 68, 74%) conditions. [5]

Dandan and Erbil [6] successfully synthesized graphite liquid marbles for the first time by encapsulating graphite micropowder on water droplets and determined their evaporation periods and useful lifetimes in constant relative humidity and temperature conditions in a closed chamber. The evaporation rates of graphite liquid marbles were compared with the rates of pure water droplets in the same conditions, and it was found that they had nearly twice the lifetime of pure water droplets. Figure 2.2 and 2.3 shows the water loss at a constant different RH and comparative results shows in the relative rate of water loss decreases in presence of the higher amount of aqueous solution.

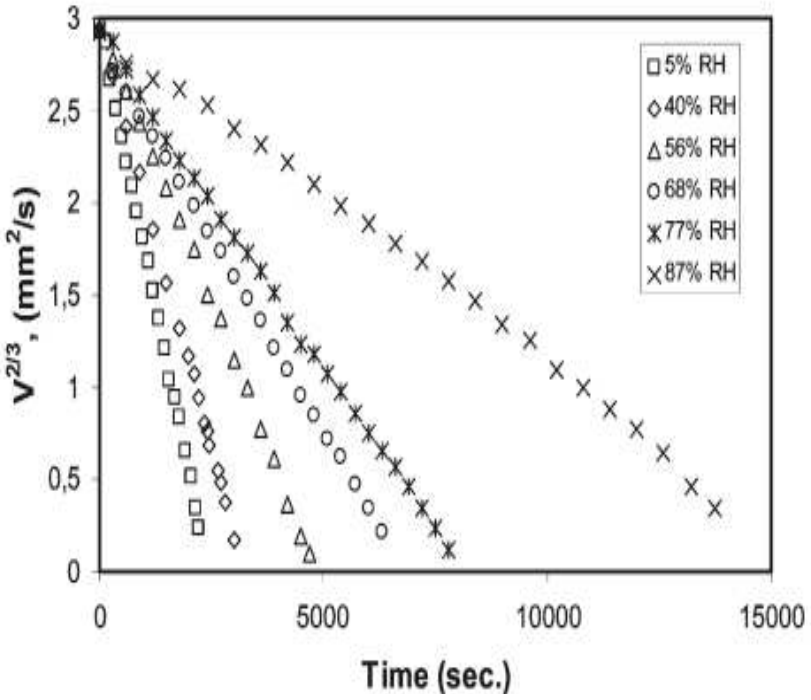

Figure 2.2 $V^{2/3}$-v/s time plot of 5 μL pure water droplets during evaporation in the closed chamber at constant relative humidity (RH=5%, 40%, 56%, 68%, 77%, 87%) conditions. [6].

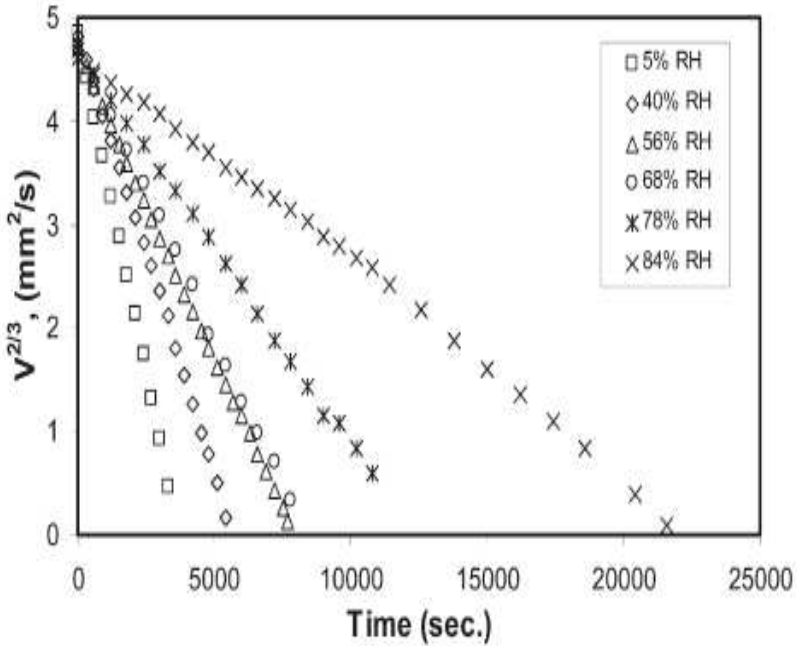

Figure 2.3 $V^{2/3}$-v/s time plot of 10 μL pure water droplets during evaporation in the closed chamber at constant relative humidity (RH=5%, 40%, 56%, 68%, 78%, 84%) conditions. [6].

Alkyl-propoxy-ethoxylate surfactant aqueous solution films were exposed to air of constant relative humidity. From the film the water loss was monitored over the time until the equilibrium was not reached by Alexandridis et al. [7]. To investigate the drying rate of the alkyl-propoxy-ethoxylate surfactants water loss data was analyzed and shown in Figure 2.8 the results shows the rate of water loss depends on the some parameters such as the air relative humidity, microstructure in the surfactant film, and the attractive interaction between the head group and water molecules at the interface.

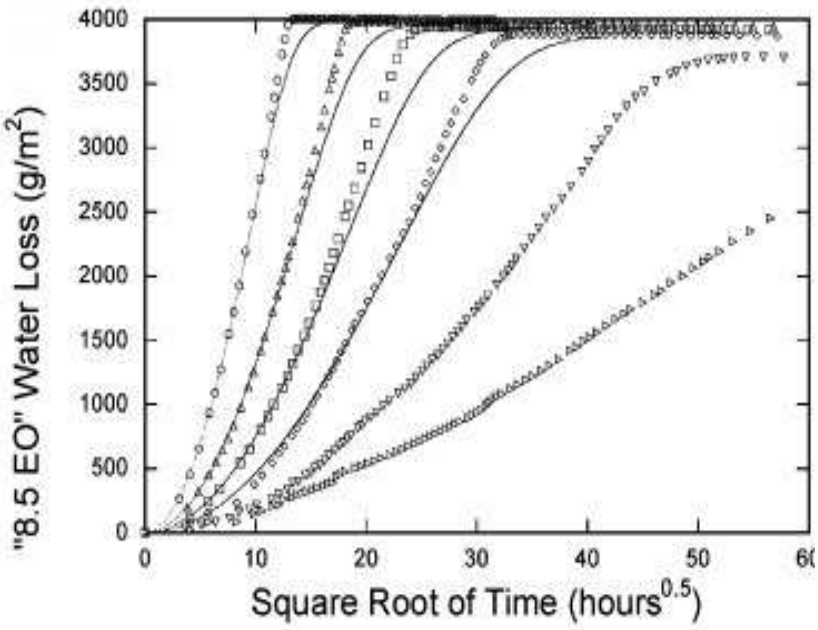

Figure 2.4 Total water loss (gram/square meters) at any given time, plotted as a function of drying time at air RH of (O) 10.9%, (4) 57.2%, (0) 75.3%, (]) 84.5%, (3) 93.8%, and (right pointing open triangle) 97.4% for the 8.5 EO. [7]

Doganci et al [8] successfully prepared liquid marbles by encapsulating graphite micropowder on aqueous sodium dodecyl sulphate (SDS) droplets and determined their total evaporation rate and buckling periods in a closed chamber having constant relative humidity

and temperature. The evaporation rates of graphite liquid marbles obtained from different concentration of SDS droplets and the results compared with the graphite liquid marbles from pure water and the results shown in Figure 2.5.

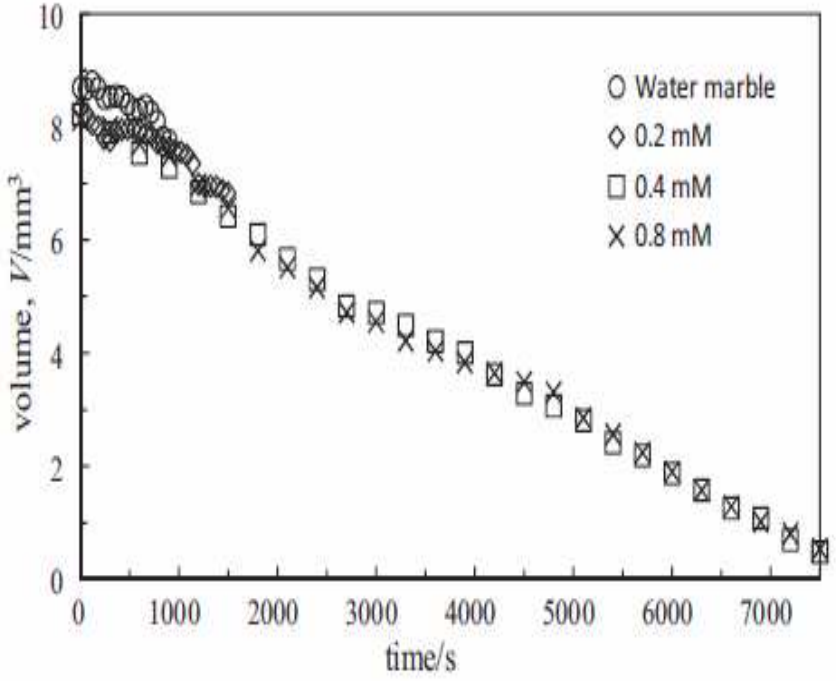

Fig. 2.5**.**Variation of the volume of graphite-stabilized liquid marbles with time for marbles made of pure water or 0.2, 0.4 and 0.8 mM SDS during evaporation in a closed chamber (Doganci et al. 2011) [8] .

Dandan et al. (2011) [9] studied the effect of SDS anionic surfactant concentration on the diffusion-controlled evaporation rate of aqueous solution drops placed on TEFLON–FEP substrate with 11 different SDS concentrations and the results shown in the Figure 2.6.

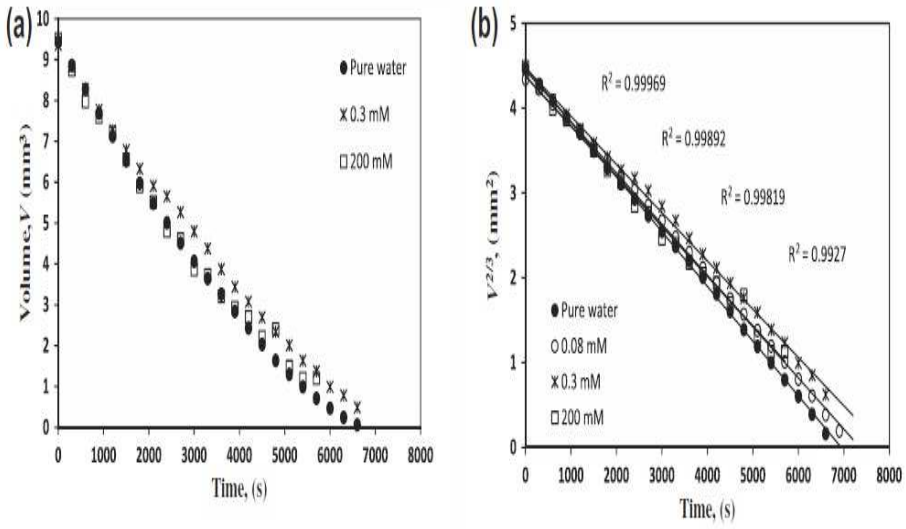

Fig. 2.6.(a) Volume change with time of pure water drop and two indicative aqueous SDS drops having concentrations of 0.3 and 200 mM; (b) V2/3–time plot of pure water drop and three indicative aqueous SDS drops having concentrations of 0.08, 0.3 and 200 mM with time during evaporation in the closed chamber at constant relative humidity of 54–57%. [9]

Rodríguez et al., [10] successfully studied the evaporation behavior of solutions of an amphiphilic polymer, phosphonated polybutadiene in toluene and in water the vapor pressure and evaporation rate measurements. The polymer reduces the vapor pressure and evaporation rate of toluene, while the opposite effect was observed in aqueous solutions as shown n the Figure 2.7.

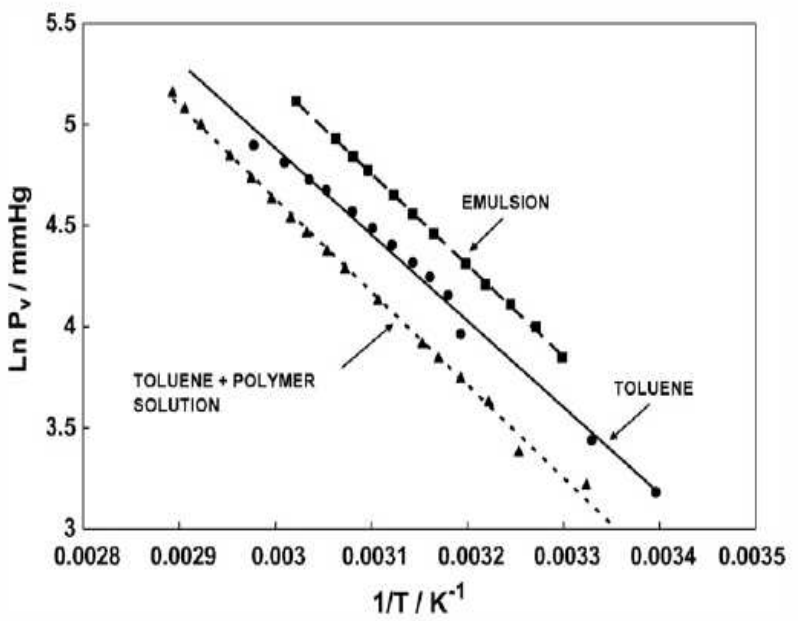

Fig. 2.7.Neperian logarithm of the vapor pressure (in mmHg) of pure toluene (●), of the toluene PPB solution obtained by rupture of the emulsion (▲) and the entire emulsion (■), as a function of the inverse of the absolute temperature [10].

2.3 Remarks

So from the above literature, it can be concluded the evaporation rate is totally depends on the relative humidity, temperature, and the presence of additives such as surfactants and polymer molecules and so on. Normally, at the higher RH as the water vapor % in the environment is high so evaporation rate successively decreases but in the presence of surfactants especially in the monomer form the evaporation rate decreases because of the tight binding of surface water molecules through electrostatic force with head groups of monomer surfactant molecules.

2.3 Objectives

The research objective can be broadly divided into following sub-sections:

- ✓ To investigate the evaporation mechanism of water in the presence of cationic and anionic surfactant solutions at ambient temperature and of controlled relative humidity.
- ✓ Effect of the electrolyte on the evaporation of water in the presence of ionic surfactants.

2.4 Organization of the thesis

In the thesis we have started with a brief introduction to effect of surfactant on evaporation of water. Then we have given some literature review and the basis and motivation of the project work. The materials and method section comes next where all the materials and their relevant properties have been specified in detail. The experimental methods adopted are explained clearly. The results and discussion part is done later and finally the conclusion of the project work.

Chapter 3

Experimental Procedure

3.1 Materials

The cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic surfactant sodium lauryl sulphate (SLS) are purchased from Sigma–Aldrich chemicals, Germany (Cat no. 2681 and pure 99.5% respectively) and used without any further purification.

3.2 Humidity Cabinet

Figure 3.1 Humidity Cabinet

The instrument was design with double walled, inner made out stainless steel sheet. The gap was filled by glass wool for temperature, insulator. To maintain uniform constant humidity and temperature a circulator fan also provided. Temperature range starts from ±22ºC. Humidity was created by generating steam by heating water in a stainless steel

reservoir by an immersion heater and subsequently condensation in circulation air. The humidity is controlled by a humidistat from atmospheric humidity to 95%±3% RH [11].

3.3 Methods

Table3.1. CMC data of used surfactants

Surfactants	CMC (mM)
CTAB	0.96
SLS	9

6 small petri dishes were taken, washed properly and put inside the dryer for drying. After drying, the petri dishes were stored in a clean place.

25 ml stock solution of 5mM concentration was prepared for CTAB.

Using the stock solution, 3 ml each of 0.5 mM, 0.7 mM, 0.96 mM, 1 mM and 2 mM concentration solutions were prepared. Since the CMC for CTAB is 0.96 mM, 2 concentrations were taken below the CMC (i.e.<0.96 mM) and two concentrations were taken above the CMC (i.e. >0.96 mM). In another petri dish, pure water without any surfactant was taken. Weights of the empty petri dishes and with solution were noted. The petri dishes were kept in air as well as in the humidity cabinet. Temperature and humidity varied under the ambient conditions. Inside the humidity cabinet, temperature and humidity were adjusted as per the requirement for the experiments. The petri dishes were taken out at constant intervals and their weights were noted. Water lost during the constant time intervals were calculated.

The same process was repeated for SLS. Since the CMC of SLS is 9mM, the experiments were carried out at 5mM, 10 mM, 15 Mm and 20 mM for SLS.

To observe the effect of electrolytes on evaporation in presence of surfactants, experiments were carried out for CTAB and SLS using sodium chloride as the electrolyte. Sodium

chloride stock solution of 200 mM concentration was prepared. 0.5 mM CTAB were taken in 4 petri dishes. NaCl of 10 mM, 20 mM and 50 mM were added to the first three petri dishes respectively. No electrolyte was added to the fourth petri dish. In another petri dish, mili-q-water was taken as a standard. The petri dishes were kept in air as well as in the humidity cabinet. Temperature and humidity varied under the ambient conditions. Inside the humidity cabinet, temperature and humidity was adjusted as per the requirement and was kept constant. The petri dishes were taken out at constant intervals and their weights were noted. Water lost during the constant time intervals were calculated.

The amount of water loss was calculated as,

Water loss = Initial weight of sample – Final weight

And the total water loss was calculated by taking summation of water loss at different time intervals for the entire time duration.

Total water loss =∑ (water loss at interval 1+ water loss at interval 2+- - - - + water loss at interval n)

Chapter 4

Results & Discussions

When a surfactant molecule is added to water the hydrophilic head group is a medium of similar polarity of itself but the hydrophobic tail group is not. For this reason it tends to distribute itself between the bulk solution and the interface between water and air. At the interface the tail group is directed towards the air but the head group remains inside water.When more and more surfactant molecules are added to the solution , it eventually becomes more energetic in the bulk solution rather than being adsorbed further at the interface. The concentration at which the monomeric form, in which the surfactant exists in very dilute solution, aggregates to form a surfactant cluster is called critical micelle concentration (CMC) [3] and the surfactant cluster is called micelle. A micelle molecule has its hydrophilic head group directed into the bulk solution and hydrophobic group towards the inner space of micelle. Inside the micelle, no water molecule is present.

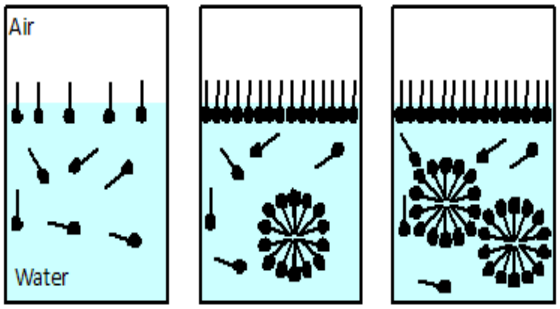

Figure 4.1.Formation of Micelle in aqueous solution

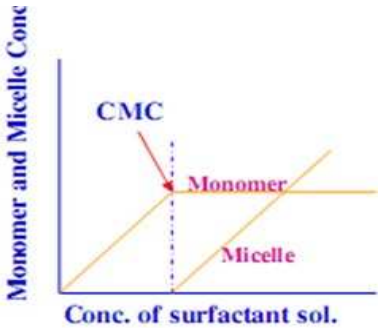

Figure 4.2.Concentration of surfactants vs. Monomer and Micelle concentration in aqueous solution

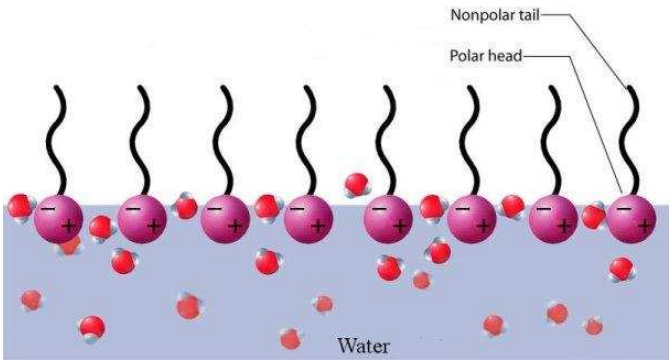

Figure 4.3 Surfactant molecules arranged on an air- water interface

Surfactant is a molecule with a hydrophobic "tail" and a hydrophilic "head". When surfactant concentration is less than critical micelle concentration (CMC), the surfactant molecules get arranged as shown in Figure 4.3. The tails are hydrophobic, and their exposure to air is favored over their exposure to water. Since the heads are hydrophilic, the head-water interaction is more favorable than air-water interaction. For concentration less than critical micelle concentration (CMC), the surfactant molecules execute a random motion on the air-water interface. The density of the surfactant molecules increases upon reducing the surface area.

With increase in time for pure water water loss increases. For a particular surfactant solution, with increase in time water loss increases but less as compared to pure water. But comparison of different surfactant concentration (5mM, 10mM, 15mM and 20mM of SLS) or (0.5mM, .96mM, 2mM and 5mM for CTAB) through with increase in time water loss increases but with increase in surfactant concentration water loss decreases.

4.1. Effect of anionic surfactant on evaporation of water molecule:

In Figure 4.4 the graph represents effect of surfactant of evaporation of water by using SLS surfactant. As mentioned above section the evaporation was decreased for the bulk present at

the interface. In this Figure 4.4 the water loss in SLS solution as compared to normal water is less.

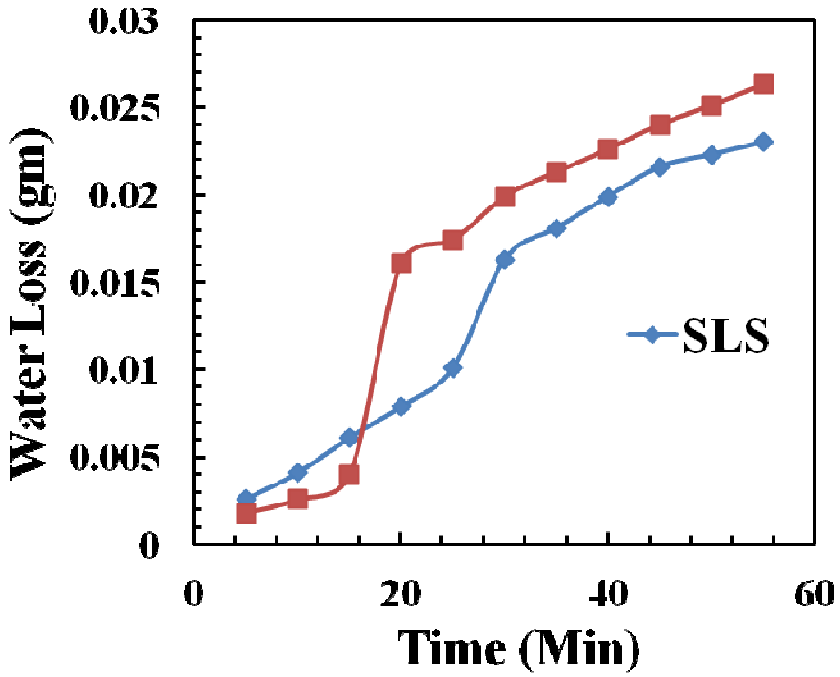

Figure 4.4.Effect of anionic surfactant on evaporation of water in 20mM SLS concentration

In Figure 4.4 here the graph represents evaporation of water by using SLS solution. As shown in the graph there are different types of concentration. The graph shows that 15mM concentration has less water loss as compared with other concentration.

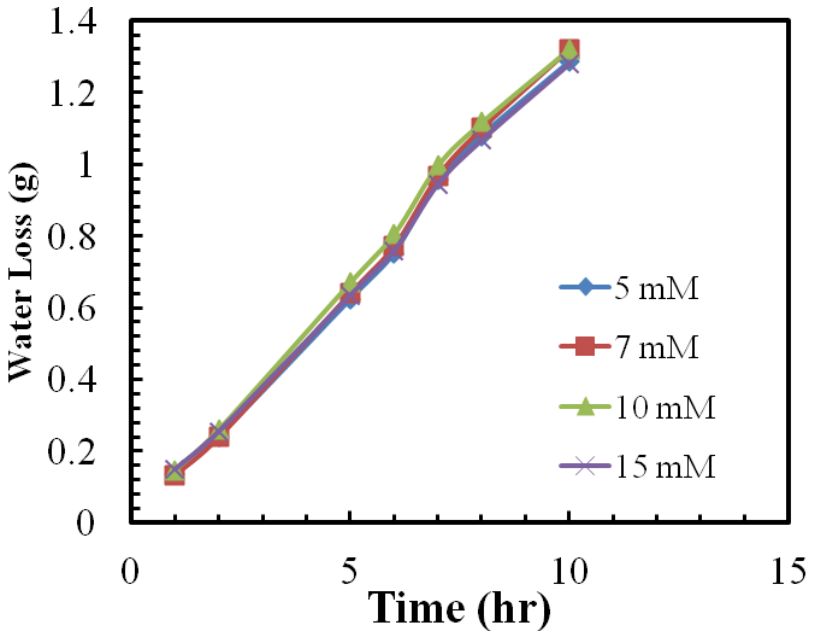

Figure 4.5.Effect of anionic surfactant (SLS) on the evaporation of water.at 15mM.

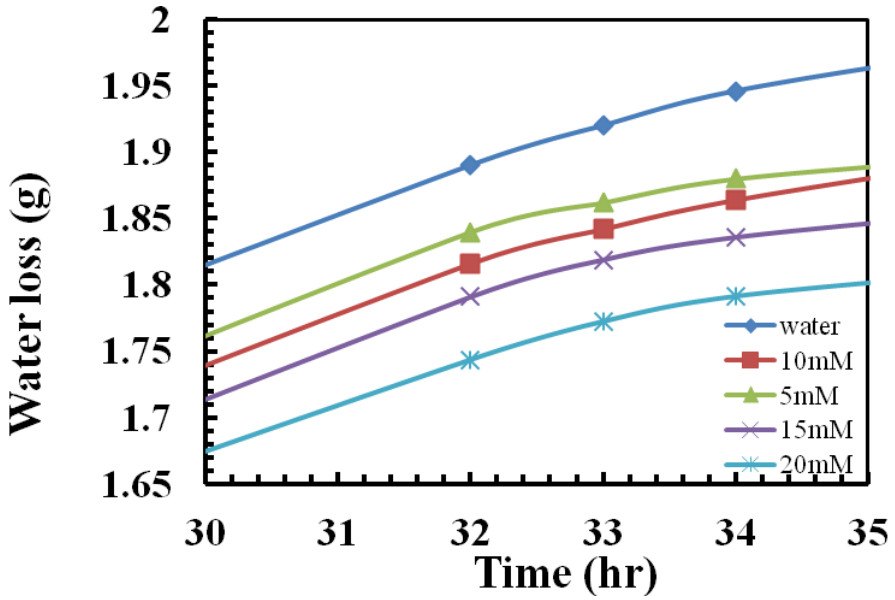

Figure 4.6.Effect of anionic surfactant (SLS) on the evaporation of water.

In figure 4.5 and 4.6 shows the difference of water loss. Here it clearly shows that how water loss decrease with increase the concentration of the surfactant. This was done because

of the monomer of the surfactant. Monomers cover the interface which does not allow the water molecules easily to vaporize. In figure no 4.6 if we compare the 20mM concentration and water then the graphs shows that the water loss was more in normal water as compared to 20mM surfactant. Similarly if we compared 20mM to other concentration like 5mM, 10mM, and 15mM there also shows that the water loss was more as compared to 20 mM.

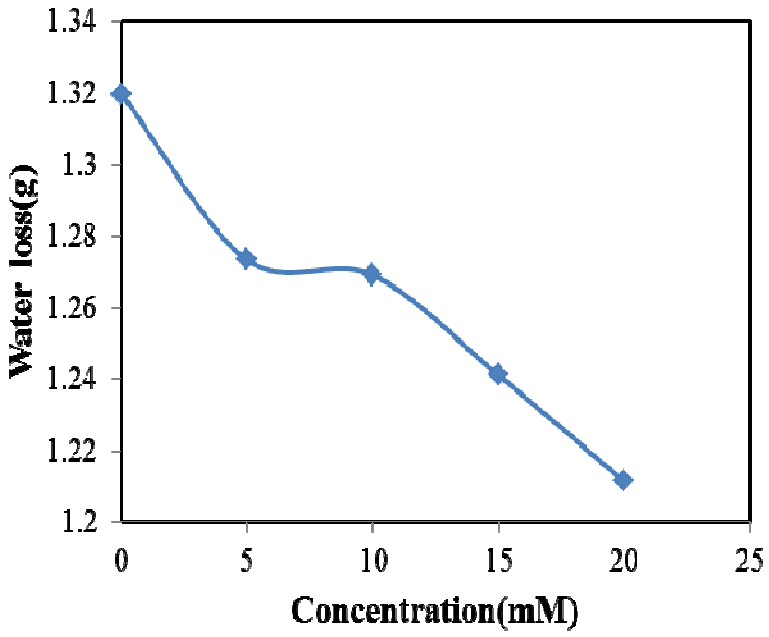

Figure 4.7 Effect of anionic surfactant (SLS) on the evaporation of water at 20hr

4.2 Effect of cationic surfactant on evaporation of water molecule

In Figure 4.9 the slope of the graph shows that the water loss of the 5mM concentration was less as compared to others. If we compare Figure 4.6 (SLS) and 4.9 (CTAB) it can be concluded that CTAB was linearly clear slope as compared to SLS. CTAB has 16 hydrocarbons and SLS has 12 hydrocarbons. So that the packing bond between CTAB was more.

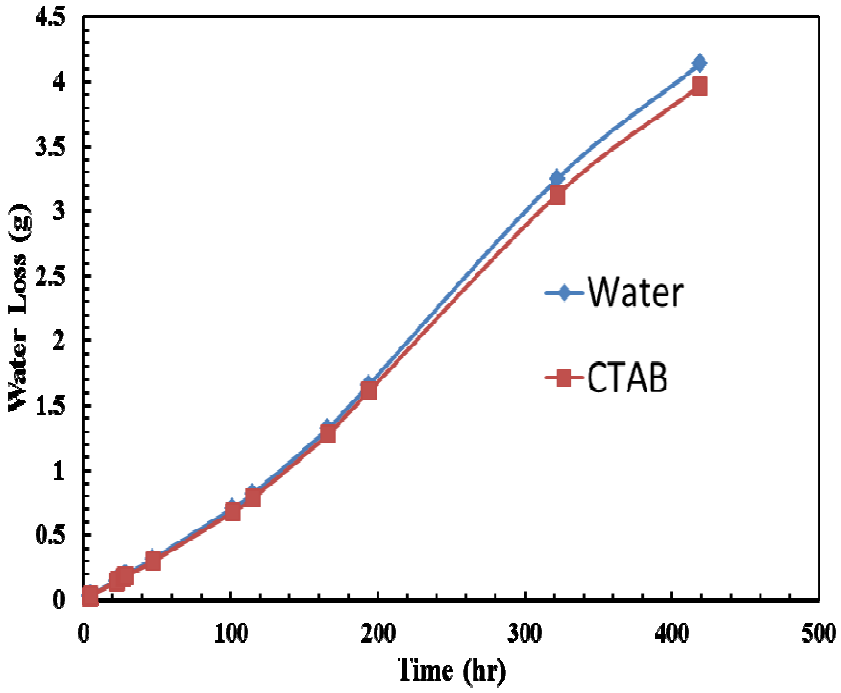

Figure 4.8.Effect of cationic surfactant (CTAB) on the evaporation of water.

In Figure 4.8 here if we compared the water loss of normal water and CTAB concentration we got that the water loss in CTAB was less as compared to water.

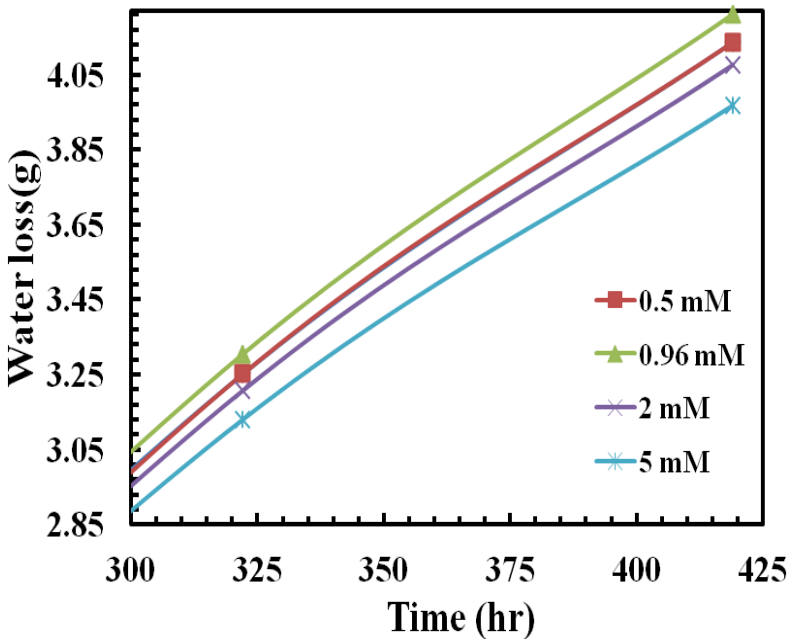

Figure 4.9 Effect of cationic surfactant (CTAB) on the evaporation of water.

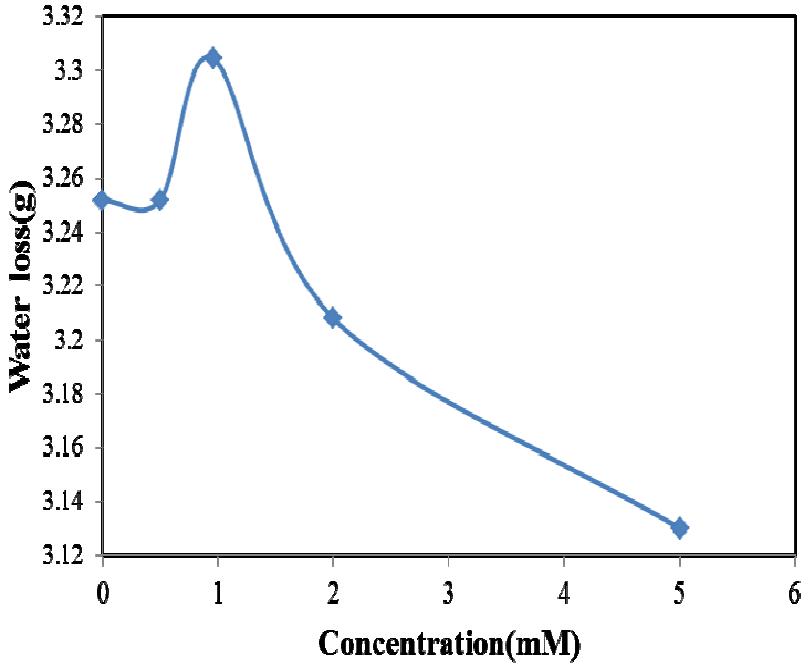

Figure 4.10 Effect of cationic surfactant (CTAB) on the evaporation of water at time 322hr.

4.3 Effect of electrolyte on evaporation of water in presence of cationic and anionic surfactant

When the ionic surfactant are adsorbed at air-liquid interface the repulsive force, an electrostatic repulsive force between the head groups of the absorber molecules are there. The presence of electrolyte reduces the repulsive interaction between the charged head group of monomers surfactant molecules solution. So due to the decrease in repulsive force CMC value of the surfactant solution also decreased in repulsive.

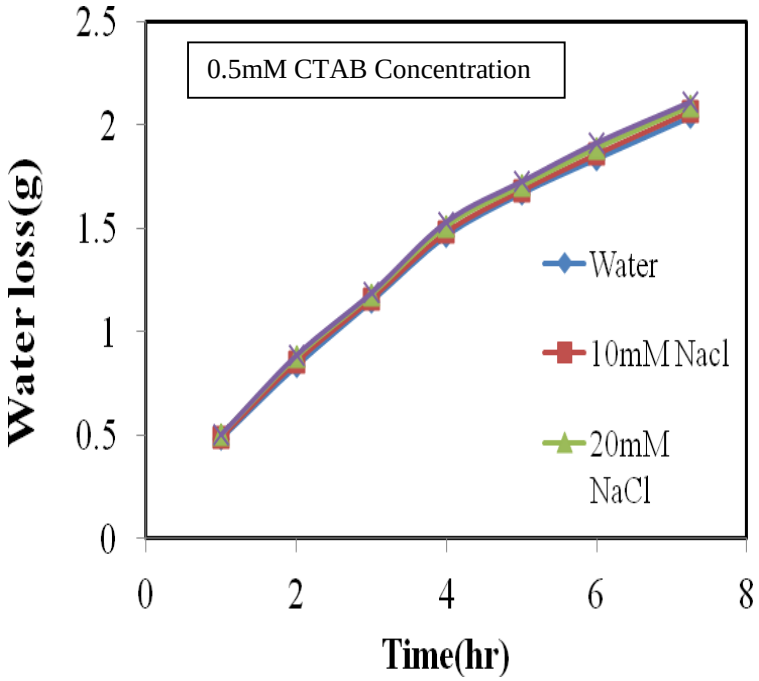

Figure 4.11 Effect of electrolyte (NaCl) on evaporation of water in presence of cationic surfactant (CTAB).

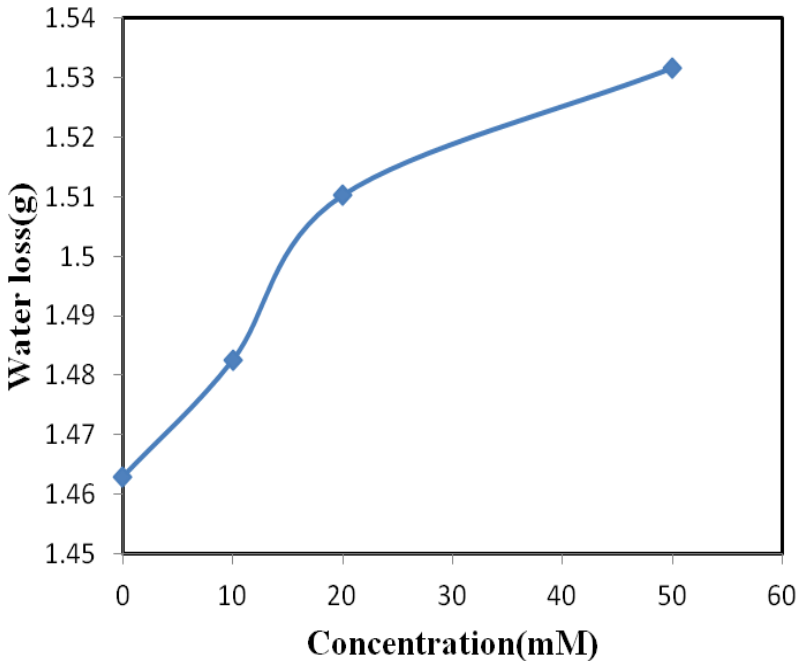

Figure 4.12 Effect of electrolye (NaCl) on evaporation of water in presence of cationic surfacatant (CTAB) at 4hrs.

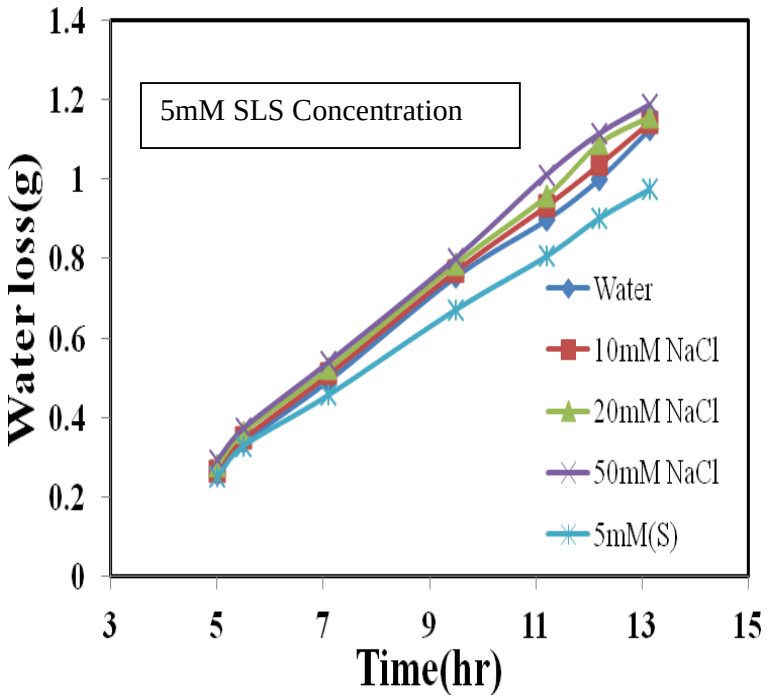

Figure 4.13 Effect of electrolyte (NaCl) on evaporation of water in presence of anionic surfactant (SLS)

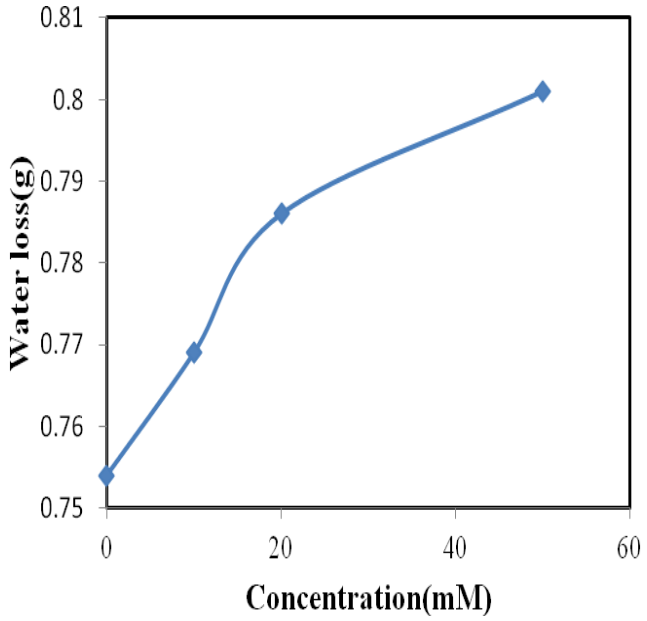

Figure 4.14 Effect of electrolyte (NaCl) on evaporation of water in presence of anionic surfactant (SLS) 9.5 hr

In Figure 4.11 and 4.13 shows the evaporation of water with increasing electrolyte (NaCl) concentration in the presence of both surfactants (CTAB and SLS). For this study low (below CMC) surfactant concentration is used and the results show with increasing the electrolytes concentration the evaporation is increases compare to the same concentration surfactant solution without any electrolytes for both the surfactant solution. In the previous literature shows in the presence of electrolytes, the CMC of the surfactant solution decreases. Therefore, it is expected in the presence of electrolytes as the CMC is decreases, so even at the low surfactant concentration (below CMC for pure surfactant), the surfactant concentration in bulk solution increases. So at the interface monomer surfactant concentration is decreases. Therefore, there will be loose packing of the monomer surfactant molecule. SO the evaporation increases compare to the same surfactant concentration solution in the absence of electrolytes.

Chapter 5

Conclusions

5. Conclusions

It was observed that the water loss because of evaporation of pure water is less compared to that in the presence of surfactants. Water evaporation further decreases with the increase in surfactant concentration.

As compared the water evaporation in the presence of CTAB and SLS, CTAB shows less water loss as compared to SLS.

In electrolyte experiment, the low (below CMC) surfactant concentration is used and the results show with increasing the electrolytes the evaporation increases compare to the same concentration surfactant solution without any electrolytes for both the surfactant solution, probably because of less number of surfactant molecule available at the inter face, as CMC value reduces to a lower concentration.

5.1. Future Work

The effect of other surfactants on evaporation of water can be studied. Also evaporation of water in presence of varying concentrations of surfactants and electrolytes can be studied.

Chapter 6

References

6. References

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